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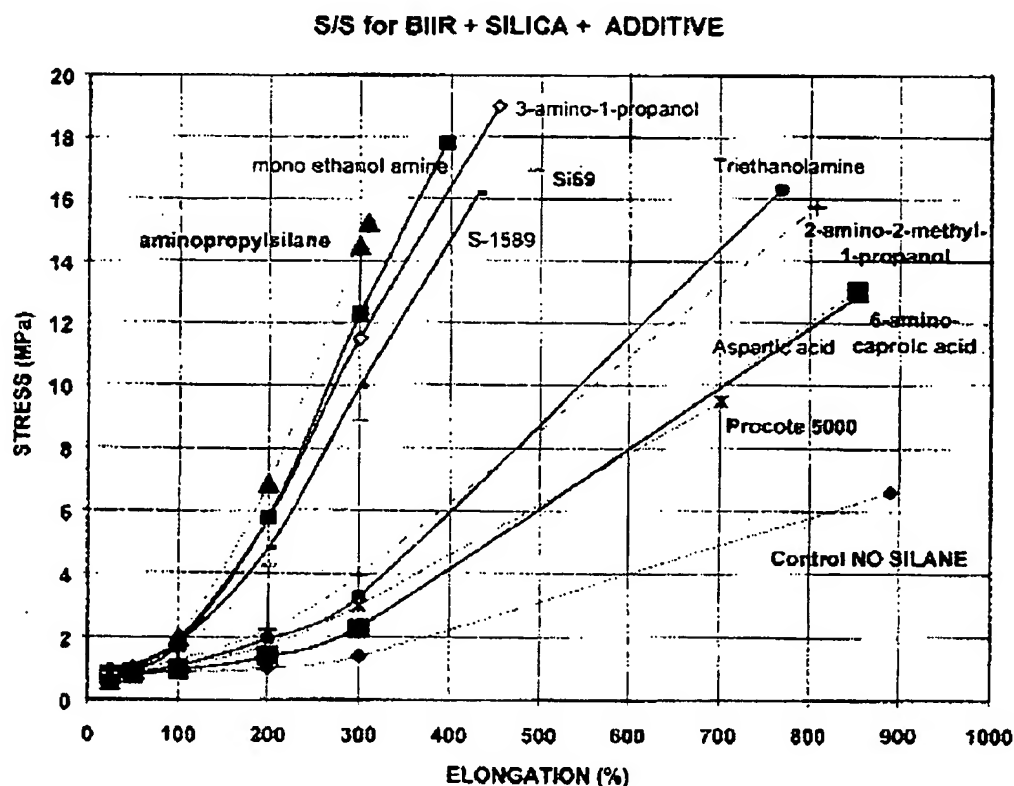
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(54) Titre : ELASTOMERES A BASE DE COMPOSES BUTYLES, CONTENANT UNE CHARGE

(54) Title: FILLED ELASTOMERIC BUTYL COMPOUNDS



(57) Abrégé/Abstract:

The invention provides a process for preparing a filled halobutyl elastomer, which comprises mixing a halobutyl elastomer, particles of filler and an additive containing both amino and alcohol functional groups, and curing the filled elastomer with sulfur or other curative systems. This invention has the advantages of (a) not evolving alcohol either during the manufacture or subsequent use of the article manufactured from the compound, and (b) significantly reducing the cost of the compound.

**ABSTRACT.**

5 The invention provides a process for preparing a filled halobutyl elastomer, which comprises mixing a halobutyl elastomer, particles of filler and an additive containing both amino and alcohol functional groups, and curing the filled elastomer with sulfur or other curative systems. This invention has the advantages of (a) not evolving alcohol either during the manufacture or subsequent use of the article manufactured from the compound, and (b) significantly reducing the cost of the compound.

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## **FILLED ELASTOMERIC BUTYL COMPOUNDS**

### **Field of the Invention:**

- 5 The present invention relates to halogenated butyl elastomers, in particular bromobutyl elastomers.

### **Background of the invention:**

- 10 It is known that reinforcing fillers such as carbon black and silica greatly improve the strength and fatigue properties of elastomeric compounds. It is also known that chemical interaction occurs between the elastomer and the filler. For example, good interaction between carbon black and highly unsaturated elastomers such as polybutadiene (BR) and styrene butadiene copolymers (SBR) occurs because of the  
15 large number of carbon-carbon double bonds present in these copolymers. Butyl elastomers may have only one tenth, or fewer, of the carbon-carbon double bonds found in BR or SBR, and compounds made from butyl elastomers are known to interact poorly with carbon black. For example, a compound prepared by mixing carbon black with a combination of BR and butyl elastomers results in domains of BR, which contain  
20 most of the carbon black, and butyl domains which contain very little carbon black. It is also known that butyl compounds have poor abrasion resistance.

- Canadian Patent Application 2,293,149 shows that it is possible to produce filled butyl elastomer compositions with much improved properties by combining halobutyl  
25 elastomers with silica and specific silanes. These silanes act as dispersing and bonding agents between the halogenated butyl elastomer and the filler. However, one disadvantage of the use of silanes is the evolution of alcohol during the process of manufacture and potentially during the use of the manufactured article produced by this process. Additionally, silanes significantly increase the cost of the resulting  
30 manufactured article.

### **Summary of the Invention:**

- 35 The present invention provides a process for preparing compositions containing halobutyl elastomers in which there is enhanced interaction between the elastomer and

a filler, especially a mineral filler. The invention also provides filled halobutyl elastomer compositions which have improved properties when compared to known carbon black-filled halobutyl elastomeric compositions. In particular it provides a means to produce such filled compositions without the evolution of alcohol, and at significantly reduced cost, compared to processes known in the art.

Surprisingly, it has been discovered that certain organic compounds containing at least one basic nitrogen-containing group and at least one hydroxyl group enhance the interaction of halobutyl elastomers with mineral fillers, resulting in improved compound properties such as tensile strength and abrasion (DIN). Of particular interest are compounds containing primary amine and hydroxyl groups such as ethanolamine. These organic compounds are believed to disperse and bond the silica to the halogenated elastomers.

Accordingly, in one aspect the present invention provides a process which comprises mixing a halobutyl elastomer with a filler, especially a mineral filler, in the presence of an additive which is an organic compound which has at least one hydroxyl group and at least one basic nitrogen-containing group, and curing the resulting filled halobutyl elastomer. The resulting composition, having improved properties, forms another aspect of the invention.

The halobutyl elastomer that is admixed with the filler and the silane may be a mixture with another elastomer or elastomeric compound. The halobutyl elastomer should constitute more than 5% of any such mixture. Preferably the halobutyl elastomer should constitute at least 10% of any such mixture. In some cases it is preferred not to use mixtures but to use the halobutyl elastomer as the sole elastomer. If mixtures are to be used, however, then the other elastomer may be, for example, natural rubber, polybutadiene, styrene-butadiene or poly-chloroprene or an elastomer compound containing one or more of these elastomers.

The filled halobutyl elastomer can be cured to obtain a product which has improved properties, for instance in abrasion resistance, rolling resistance and traction. Curing can be effected with sulfur. The preferred amount of sulfur is from about 0.3 to about 2.0 parts by weight per hundred parts of rubber. An activator, for example zinc oxide, may also be used, in an amount of from about 5 parts to about 2 parts by weight. Other

ingredients, for instance stearic acid, antioxidants, or accelerators may also be added to the elastomer prior to curing. Sulphur curing is then effected in known manner. See, for instance, chapter 2, "The Compounding and Vulcanization of Rubber", of "Rubber Technology", 3<sup>rd</sup> edition, published by Chapman & Hall, 1995, the disclosure of which is incorporated by reference.

Other curatives known to cure halobutyl elastomers may also be used. A number of compounds are known to cure BIIR, for example, such as bis dienophiles (for example HVA2) phenolic resins, amines, amino-acids, peroxides, zinc oxide and the like. Combinations of the aforementioned curatives may also be used.

The mineral-filled halobutyl elastomer of the invention can be admixed with other elastomers or elastomeric compounds before it is subjected to the curing with sulphur. This is discussed further below.

#### **Detailed Description of the Invention**

The phrase "halobutyl elastomer(s)" as used herein refers to a chlorinated or brominated butyl elastomer. Brominated butyl elastomers are preferred, and the invention is illustrated, by way of example, with reference to such bromobutyl elastomers. It should be understood, however, that the invention extends to the use of chlorinated butyl elastomers.

Thus, halobutyl elastomers suitable for use in the practice of this invention include, but are not limited to, brominated butyl elastomers. Such elastomers may be obtained by bromination of butyl rubber (which is a copolymer of isobutylene and a co-monomer that is usually a C<sub>4</sub> to C<sub>6</sub> conjugated diolefin, preferably isoprene). Co-monomers other than conjugated diolefins can be used, however, and mention is made of alkyl-substituted vinyl aromatic co-monomers such as C<sub>1</sub>-C<sub>4</sub>-alkyl substituted styrene. An example of such an elastomer which is commercially available is brominated isobutylene methylstyrene copolymer (BIMS) in which the co-monomer is p-methylstyrene.

Brominated butyl elastomer typically contains from about 1 to about 3 weight percent of isoprene and from about 97 to about 99 weight percent of isobutyl ne (based upon the

hydrocarbon content of the polymer) and from about 1 to about 4 weight percent bromine (based upon the bromobutyl polymer). A typical bromobutyl polymer has a molecular weight, expressed as the Mooney viscosity (ML 1 + 8 at 125°C), of from about 28 to about 55.

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For use in the present invention the brominated butyl elastomer preferably contains from about 1 to about 2 weight percent of isoprene and from about 98 to about 99 weight percent of isobutylene (based upon the hydrocarbon content of the polymer) and from about 0.5 to about 2.5 weight percent, preferably from about 0.75 to about 2.3 weight percent, of bromine (based upon the brominated butyl polymer).

10

A stabilizer may be added to the brominated butyl elastomer. Suitable stabilizers include calcium stearate and epoxidized soybean oil, preferably used in an amount of from about 0.5 to about 5 parts by weight per 100 parts by weight of the brominated butyl rubber.

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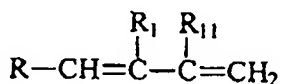
Examples of suitable brominated butyl elastomers include Bayer Bromobutyl 2030, Bayer Bromobutyl 2040 (BB2040), and Bayer Bromobutyl X2 commercially available from Bayer. Bayer BB2040 has a Mooney viscosity (RPML 1+8 @ 125°C) of  $39 \pm 4$ , a bromine content of  $2.0 \pm 0.3$  wt% and an approximate molecular weight of 500,000 grams per mole.

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The brominated butyl elastomer used in the process of this invention may also be a graft copolymer of a brominated butyl rubber and a polymer based upon a conjugated diolefin monomer. Our co-pending Canadian Patent Application 2,279,085 is directed towards a process for preparing such graft copolymers by mixing solid brominated butyl rubber with a solid polymer based on a conjugated diolefin monomer which also includes some C-S-(S)<sub>n</sub>-C bonds, where n is an integer from 1 to 7, the mixing being carried out at a temperature greater than about 50°C and for a time sufficient to cause grafting. The disclosure of this application is incorporated herein by reference. The bromobutyl elastomer of the graft copolymer can be any of those described above. The conjugated diolefins that can be incorporated in the graft copolymer generally have the structural formula :

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wherein R is a hydrogen atom or an alkyl group containing from 1 to 8 carbon atoms and wherein R<sub>1</sub> and R<sub>11</sub> can be the same or different and are selected from the group consisting of hydrogen atoms and alkyl groups containing from 1 to 4 carbon atoms.

5 Some representative non-limiting examples of suitable conjugated diolefins include 1,3-butadiene, isoprene, 2-methyl-1,3-pentadiene, 4-butyl-1,3-pentadiene, 2,3-dimethyl-1,3-pentadiene, 1,3-hexadiene, 1,3-octadiene, 2,3-dibutyl-1,3-pentadiene, 2-ethyl-1,3-pentadiene, 2-ethyl-1,3-butadiene and the like. Conjugated diolefin monomers containing from 4 to 8 carbon atoms are preferred, 1,3-butadiene and isoprene being  
10 especially preferred.

The polymer based on a conjugated diene monomer can be a homopolymer, or a copolymer of two or more conjugated diene monomers, or a copolymer with a vinyl aromatic monomer.

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The vinyl aromatic monomers which can optionally be used are selected so as to be copolymerizable with the conjugated diolefin monomers being employed. Generally, any vinyl aromatic monomer which is known to polymerize with organo-alkali metal initiators can be used. Such vinyl aromatic monomers usually contain from 8 to 20  
20 carbon atoms, preferably from 8 to 14 carbon atoms. Some examples of vinyl aromatic monomers which can be so co-polymerized include styrene, alpha-methyl styrene, various alkyl styrenes including p-methylstyrene, p-methoxy styrene, 1-vinylnaphthalene, 2-vinyl naphthalene, 4-vinyl toluene and the like. Styrene is preferred for copolymerization with 1,3-butadiene alone or for terpolymerization with both 1,3-  
25 butadiene and isoprene.

The filler is composed of particles of a mineral, and examples include silica, silicates, clay (such as bentonite), gypsum, alumina, titanium dioxide, talc and the like, as well as mixtures thereof. These mineral particles have hydroxyl groups on their surface,  
30 rendering them hydrophilic and oleophobic. This exacerbates the difficulty of achieving good interaction between the filler particles and the butyl elastomer. For many purposes, the preferred mineral is silica, specially silica prepared by the carbon dioxide precipitation of sodium silicate.

Dried amorphous silica particles suitable for use in accordance with the invention have a mean agglomerate particle size between 1 and 100 microns, preferably between 10 and 50 microns and most preferably between 10 and 25 microns. It is preferred that less than 10 percent by volume of the agglomerate particles are below 5 microns or over 50 microns in size. A suitable amorphous dried silica moreover has a BET surface area, measured in accordance with DIN (Deutsche Industrie Norm) 66131, of between 50 and 450 square meters per gram and a DBP absorption, as measured in accordance with DIN 53601, of between 150 and 400 grams per 100 grams of silica, and a drying loss, as measured according to DIN ISO 787/11, of from 0 to 10 percent by weight. Suitable silica fillers are available under the trademarks HiSil 210, HiSil 233 and HiSil 243 from PPG Industries Inc. Also suitable are Vulkasil S and Vulkasil N, from Bayer AG.

The additive contains at least one hydroxyl group, which (without being bound to any particular theory) may react with the mineral filler, and at least one group containing a basic nitrogen atom, which (without being similarly bound) may react with the active halogen in a halogenated butyl elastomer (for example with the active bromine atom in a brominated butyl elastomer). Functional groups containing -OH may be, for example, alcohols or carboxylic acids. Functional groups containing a basic nitrogen atom include, but are not limited to, amines (which can be primary, secondary or tertiary) and amides. Preferred are primary alkyl amine groups such as aminoethyl, aminopropyl and the like.

Examples of additives which give enhanced physical properties to mixtures of halobutyl elastomers and silica include proteins, aspartic acid, 6-aminocaproic acid, diethanolamine and triethanolamine. Preferably, the additive should contain a primary alcohol group and a primary amino group separated by methylene bridges, which may be branched. Such compounds have the general formula  $\text{HO-A-NH}_2$ ; wherein A represents a C1 to C20 alkylene group, which may be linear or branched.

More preferably, the number of methylene groups between the two functional groups should be between 1 and 4. Examples of preferred additives include monoethanolamine and 3-amino-1-propanol.



The amount of filler to be incorporated into the halobutyl elastomer can vary between wide limits. Typical amounts of filler range from about 20 parts to about 120 parts by weight, preferably from about 30 parts to about 100 parts, more preferably from about 40 to about 80 parts per hundred parts of elastomer. The amount of the additive used is dependent upon the molecular/equivalent weight of each specific compound. One important factor is the number/weight of nitrogen per unit weight of the compound. The level of nitrogen may range from about 0.1 to about 5 parts per hundred (phr) of halobutyl rubber, preferably from about 0.125 to about 1 phr and, more preferably, from about 0.3 to about 0.7 phr. Up to about 40 parts of processing oil, preferably from about 5 to about 20 parts, per hundred parts of elastomer, may be present. Further, a lubricant, for example a fatty acid such as stearic acid, may be present in an amount up to about 3 parts by weight, more preferably in an amount up to 2 parts by weight.

Carbon black is not normally used as a filler in the halobutyl elastomer compositions of the invention, but in some embodiments it may be present in an amount up to about 40 phr. If the mineral filler is silica and it is used with carbon black, the silica should constitute at least 55% by weight of the total of silica and carbon black. If the halobutyl elastomer composition of the invention is blended with another elastomeric composition, that other composition may contain carbon black as a filler.

The halobutyl elastomer, filler and additive are mixed together, suitably at a temperature in the range of from about 25 to about 200°C. It is preferred that the temperature in one of the mixing stages be greater than about 60°C, and a temperature in the range of from about 90 to about 150°C is particularly preferred. Normally the mixing time does not exceed about one hour; a time in the range from about 2 to 30 minutes is usually adequate. The mixing is suitably carried out on a two-roll mill mixer, which provides good dispersion of the filler within the elastomer. Mixing may also be carried out in a Banbury mixer, or in a Haake or Brabender miniature internal mixer. An extruder also provides good mixing, and has the further advantage that it permits shorter mixing times. It is also possible to carry out the mixing in two or more stages. Further, the mixing can be carried out in different apparatuses, for example one stage may be carried out in an internal mixer and another in an extruder.

The enhanced interaction between the filler and the halobutyl elastomer results in improved properties for the filled elastomer. These improved properties include high

tensile strength, higher abrasion resistance, lower permeability and better dynamic properties. These render the filled elastomers particularly suitable for a number of applications, including, but not limited to, use in tire treads and tire sidewalls, tire innerliners, tank linings, hoses, rollers, conveyor belts, curing bladders, gas masks, pharmaceutical enclosures and gaskets.

In a preferred embodiment of the invention, bromobutyl elastomer, silica particles, additive and, optionally, processing oil extender are mixed on a two-roll mill at a nominal mill temperature of 25°C. The mixed compound is then placed on a two-roll mill and mixed at a temperature above 60°C. It is preferred that the temperature of the mixing is not too high, and more preferably does not exceed about 150°C, since higher temperatures may cause curing to proceed undesirably far and thus impede subsequent processing. The product of mixing these four ingredients at a temperature not exceeding about 150°C is a compound which has good stress/strain properties and which can be readily processed further on a warm mill with the addition of curatives.

The filled halobutyl rubber compositions of the invention, and in particular filled bromobutyl rubber compositions, find many uses, but mention is made particularly of use in tire tread compositions. Important features of a tire tread composition are that it shall have low rolling resistance, good traction, particularly in the wet, and good abrasion resistance so that it is resistant to wear. Compositions of the invention display these desirable properties. Thus, an indicator of traction is  $\tan \delta$  at 0°C, with a high  $\tan \delta$  at 0°C correlating with good traction. An indicator of rolling resistance is  $\tan \delta$  at 60°C, with a low  $\tan \delta$  at 60°C correlating with low rolling resistance. Rolling resistance is a measure of the resistance to forward movement of the tire, and low rolling resistance is desired to reduce fuel consumption. Low values of loss modulus at 60°C are also indicators of low rolling resistance. As is demonstrated in the examples below, compositions of the invention display high  $\tan \delta$  at 0°C, low  $\tan \delta$  at 60°C and low loss modulus at 60°C.

The filled halobutyl elastomers of this invention can be further mixed with other rubbers, for example natural rubber, butadiene rubber, styrene-butadiene rubber and isoprene rubbers, and compounds contain these elastomers.

The invention is further illustrated in the following examples and the accompanying Figure 1.

Description of tests:

- 5    *Abrasion resistance:* DIN 53-516 (60 grit Emery paper)

*Dynamic Property Testing*

Dynamic testing (Tan  $\delta$  at 0°C and 60°C, Loss modulus at 60°C) were carried out using the Rheometrics RSA II. The RSA II is a dynamic mechanical analyzer for  
10    characterizing the properties of vulcanized elastomeric materials.

The dynamic mechanical properties give a measure of traction with the best traction usually obtained with high values of Tan  $\delta$  at 0°C. Low values of Tan  $\delta$  at 60°C., and in particular, low loss modulus at 60°C. are indicators of low rolling resistance.

- 15    *Cure rheometry:* ASTM D 52-89 MDR2000E Rheometer at 3° arc and 1.7 Hz

*Permeability:* ASTM D 14-34

The invention is further illustrated in the following examples.

20

Description of Ingredients and General Mixing Procedure:

Hi-Sil 233 - silica - a product of PPG

Sunpar 2280 - paraffinic oil produced by Sun Oil.

- Pro-Cote® 5000 is a low molecular weight, chemically modified soy polymer designed  
25    as a multi-functional coating additive and binder. It is produced by Protein Technologies International, located in St Louis, MO, USA.

The brominated butyl elastomer, silica, oil and a bonding compound were mixed on a 6" X 12" two-roll mill with the rolls running at 24 and 32 rpm. The mill roll was set at 25°C,  
30    with a total incorporation time of 10 minutes. The mixed compounds were then "heat treated" for a further 10 minutes with the roll temperature at 110°C. The final rubber temperature was 125°C. Curatives were then added to the cooled sample with the mill at 25°C.

**Exempl 1**

A number of different additives containing hydroxyl and nitrogen atoms were compared with 3 different silane additives commonly used in elastomer silica compounds. A compound containing no bonding agent was also prepared, as a control sample.

5

The bonding agents used were :

- (i) 6-Amino caproic acid ;
- (ii) Aspartic acid ;
- 10 (iii) Pro-Cote® 5000 (soy protein) ;
- (iv) Triethanolamine ;
- (v) 2-Amino-2-methyl-1-propanol ;
- (vi) 3-Amino-1-propanol ; and
- (vii) Monoethanolamine.

15

The three commonly used silanes used for comparison purposes were :

- (a) Amino propyl triethoxy silane ;
- (b) Si69, bis[3-(triethoxysilyl)propyl]- tetrasulfane  
20  $[(C_2H_5O)_3Si-(CH_2)_3-S_4-(CH_2)_3-Si(OC_2H_5)_3]$  ; and
- (c) Silquest 1589, bis[3-(triethoxysilyl)propyl]- disulfane  
 $(C_2H_5O)_3Si-(CH_2)_3-S_2-(CH_2)_3-Si(OC_2H_5)_3]$ .

25 Brominated isoprene isobutylene rubber (BIIR) was mixed with the additive, 60 parts per hundred rubber (phr) of silica filler (Hisil 233) and 10phr of oil extender (Sunpar 2280) on a 6" x 12" mill under the mixing conditions described above. Identical curative ingredients (1 phr of stearic acid and sulfur, and 1.5phr. of ZnO) were then added on a cool mill to each of the compounds. The compounds were then cured for either  $t_c(90) + 10$  minutes at 170°C (for DIN Abrasion testing) or  $t_c(90) + 5$  minutes at 170°C and  
30 tested. Table 1 gives the product compositions, and physical property data for three commonly used silanes and for a compound containing no filler bonding agent.

The data in Table 1 clearly shows the effect of adding silanes to assist in the dispersion and bonding of the filler in the brominated butyl elastomer. The ratio M300/M100 is  
35 commonly used as a relative measure of the degree of filler reinforcement in an

elastomer compound (the higher the ratio the higher the reinforcement). M300 / M100 for the control (no silane) is 1.6 and for silanes ranges from 5.4 to 7.3.

Table 2 gives the product compositions and physical property data for representative additives used in the practice of this invention.

The data in Table 2 show that the products of this invention have M300 / M100 values of between 2.4 and 7.0. In comparison with the data in Table 1, this shows that all the additives in Table 2 provide some degree of reinforcement. Figure 1, a plot of the stress strain data, also shows this reinforcement.

Examination of the DIN Abrasion test data show that the additives improve wear, although the sample containing no bonding agent was too soft to test. It is also noteworthy that preferred additives, exemplified by 3-amino-1-propanol and mono-ethanolamine, show much higher values for  $\tan \delta$  at 60°C and much lower values for the loss modulus at 60°C than the other additives.

### Example 2

Comparisons were made for mono-, di-, and tri- ethanolamine in a compound containing BIIR + Hi-Sil 233.

Brominated isoprene isobutylene rubber (BIIR) was mixed with the various additives and 60phr of silica filler (Hisil 233) on a 6" x 12" mill under the mixing conditions described above. Identical curative ingredients, 1 phr of stearic acid and sulfur, and 1.5phr. of ZnO, were then added on a cool mill to each of the compounds. The compounds were then cured for either  $t_c(90) + 10$  minutes at 170°C (for DIN Abrasion testing) or  $t_c(90) + 5$  minutes at 170°C and tested. Table 3 gives the product compositions, and physical property data in comparison with amino-propyl triethoxy silane.

The M300 / M100 data in Table 3 show that the primary is better than the secondary which is better than the tertiary amine in dispersing and bonding the filler to the BIIR. The mono-ethanolamine also has the highest  $\tan \delta$  at 60°C. and the lowest values for the loss modulus at 60°C.

**Exempl 3:**

To investigate the effect of the concentration of the dispersing and bonding agent, the concentration of 3-amino-1-propanol was varied from 1.4 to 2.8 to 5.4phr.

5 Brominated isoprene isobutylene rubber (BIIR) was mixed with 3-amino-1-propanol and 60phr of silica filler (Hisil 233) on a 6" x 12" mill under the mixing conditions described above. Identical curative ingredients, 1 phr. of stearic acid and sulfur, and 1.5phr. of ZnO, were then added on a cool mill to each of the compounds. The compounds were  
10 then cured for either  $t_c(90) + 10$  minutes at 170°C (for DIN Abrasion testing) or  $t_c(90) + 5$  minutes at 170°C and tested. Table 4 gives the product compositions, and physical property data in comparison with amino-propyl triethoxy silane.

The data in Table 4 show that a level of 2.8phr. is superior to that of either 1.4 or 5.4  
15 phr. of 3-amino-1-propanol.

**Example 4.**

To investigate the effect of the number of methylene ( $-\text{CH}_2-$ ) groups between the amine and the alcohol functional groups, monoethanolamine, 3-amino-1-propanol, and 5-  
20 amino-1-pentanol were compared with the same equivalent number of amino groups. The data is shown in Table 5.

The data in Table 5 shows poorer properties for 5- amino-1-pentanol compared to monoethanolamine and 3-amino-1-propanol.  
25

TABLE 1

<b>CODE: 00CW</b>	<b>96</b>	<b>106</b>	<b>105</b>	<b>93</b>
Additive	(control)	(c)	(b)	(a)
Additive amount (phr.)	0	8.6	9.8	8
<b>STRESS STRAIN (Die C DUMBELLS, cure tc90+5 @ 170°C., tested @ 23°C)</b>				
Hard. Shore A2 Inst. (pts.)	61	62	59	51
Ultimate Tensile (MPa)	6.6	16.2	16.9	15.2
Ultimate Elongation (%)	890	431	494	309
Stress @ 50 (MPa)	0.89	1.13	1.03	0.95
Stress @ 100 (MPa)	0.87	1.83	1.59	2
Stress @ 200 (MPa)	1.01	4.8	4.23	6.89
Stress @ 300 (MPa)	1.39	9.94	8.88	14.5
M300/M100	1.6	5.43	5.58	7.3
<b>DIE C TEAR (cured tc90+5 @ 170°C., tested @ R.T.)</b>				
Tear Strength (kN/m)	18.7	25.8	30.3	18.8
<b>DIN ABRASION (cure tc90+5 @ 170°C.,)</b>				
Abrasion Volume Loss (mm <sup>3</sup> )	NR sample deformed	235	198	230
<b>RSA II, TEMPERATURE SWEEP (2°C/min, 60sec soak, 70rad/s, cured tc90+5 @ 170°C)</b>				
Tan delta@ 0°C.	0.32	0.65	0.66	0.77
Tan delta@ +60°C.	0.10	0.16	0.16	0.11
Loss modulus@ +60°C.	1.90	0.79	0.63	0.45
<b>MDR CURE CHARACTERISTICS (1.7Hz, 170deg.C., 3 arc, 60 mins.)</b>				
MH (dN.m)	22.8	34.5	32.8	38.4
ML (dN.m)	14.7	6.7	7.3	11.8
ts 1 (min)	1.02	0.72	0.54	0.66
ts 2 (min)	1.98	0.9	0.66	0.84
t' 10 (min)	0.86	1.11	0.74	0.94
t' 50 (min)	5.61	5.84	2.34	3.36
t' 90 (min)	23.9	22.3	10.8	9.1
t' 95 (min)	28.6	26.2	13.1	11.0

TABLE 2

<b>CODE: 00CW</b>	<b>100</b>	<b>107</b>	<b>95</b>	<b>108</b>	<b>98</b>	<b>99</b>	<b>101</b>
Additive	(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)
Additive amount (phr.)	4.8	4.8	8	5.4	3.25	2.7	2.2
<b>STRESS STRAIN (Die C DUMBELLS, cure tc90+5 @ 170°C., tested @ 23°C.)</b>							
Hard. Shore A2 Inst. (pts.)	61	60	58	62	64	54	50
Ultimate Tensile (MPa)	13.1	12.9	9.5	16.3	15.8	19.0	17.8
Ultimate Elongation (%)	853	856	702	768	807	453	395
Stress @ 50 (MPa)	0.82	0.82	0.88	0.86	1.02	1.03	0.91
Stress @ 100 (MPa)	0.94	0.94	1.04	1.09	1.27	1.9	1.76
Stress @ 200 (MPa)	1.4	1.39	1.75	1.95	2.23	5.74	5.77
Stress @ 300 (MPa)	2.28	2.32	2.99	3.27	3.86	11.48	12.27
M300/M100	2.4	2.47	2.9	3.00	3.1	6.0	6.97
<b>DIE C TEAR (cured tc90+5 @ 170°C., tested @ R.T.)</b>							
Tear Strength (kN/m)	48.3	56.0	27.0	51.9	55.2	29.5	25.0
<b>DIN ABRASION (cure tc90+5 @ 170°C.)</b>							
Abrasion Volume Loss (mm <sup>3</sup> )	615	210	651	543	422	262	423
<b>RSA II, TEMPERATURE SWEEP (2°C/min, 60sec soak, 70rad/s, cured tc90+5 @ 170°C)</b>							
Tan delta@ 0°C.	0.33	0.31	0.45	0.36	0.33	0.55	0.59
Tan delta@ +60°C.	0.13	0.13	0.14	0.11	0.11	0.10	0.11
Loss modulus@ +60°C.	2.23	2.36	1.42	2.27	1.60	0.86	0.77
<b>MDR CURE CHARACTERISTICS (1.7Hz, 170deg.C., 3 arc, 60 mins.)</b>							
MH (dN.m)	29.6	30.3	25.2	38.5	34.9	42.6	37.2
ML (dN.m)	12.1	11.8	12.4	9.3	9.0	10.4	9.0
ts 1 (min)	0.72	0.66	0.96	0.6	0.9	0.48	0.66
ts 2 (min)	0.96	0.9	1.38	0.72	1.2	0.6	0.84
t' 10 (min)	0.85	0.84	1.05	0.82	1.37	0.71	0.95
t' 50 (min)	3.08	3.13	5.47	2.55	5.38	3.08	4.26
t' 90 (min)	9.6	9.6	26.4	8.5	14.6	9.5	12.3
t' 95 (min)	12.0	12.3	32.8	11.3	17.5	12.0	14.9



TABLE 3.

CODE 00CW...	217	218	219	220
Additive	(a)	(vii)	diethanolamine	(iv)
Additive amount (phr.)	8	2.2	3.9	5.4
<b>STRESS STRAIN</b> (Die C DUMBELLS, t90+5 @ 170°C., tested @ 23°C.)				
Hard. Shore A2 Inst. (pts.)	57	58	67	70
Ultimate Tensile (MPa)	16.5	18.5	20.1	17.6
Ultimate Elongation (%)	278	329	545	658
Stress @ 50 (MPa)	1.17	1.3	1.37	1.17
Stress @ 100 (MPa)	2.43	2.69	2.08	1.46
Stress @ 200 (MPa)	8.75	8.5	5.21	2.94
Stress @ 300 (MPa)	17.92	16.81	10.1	6
300M / 100M	7.4	6.2	4.9	4.1
<b>DIE C TEAR</b> (cured tc90+5 @ 170°C., tested @ R.T.)				
Tear Strength (kN/m)	19.0	27.8	42.1	47.3
<b>DIN ABRASION</b> (cure tc90+10 @ 170°C.)				
Abrasion Volume Loss (mm³)	113	90	138	145
<b>RSA II, TEMPERATURE SWEEP</b> (2°C/min, 60sec soak, 70rad/s, cured tc90+5 @ 170°C)				
Tan delta@ 0°C.	0.806	0.639	0.436	0.374
Tan delta@ +60°C.	0.109	0.105	0.096	0.085
Loss modulus@ +60°C.	0.397	1.040	1.928	2.309
<b>MDR CURE CHARACTERISTICS</b> (1.7 Hz., 3°arc, 60' @ 170°C.)				
MH (dN.m)	46.9	45.3	46.6	48.0
ML (dN.m)	16.3	12.3	10.8	12.8
ts 1 (min)	0.6	0.48	0.66	0.96
ts 2 (min)	0.78	0.54	0.9	1.26
t' 10 (min)	0.88	0.65	1.16	1.64
t' 50 (min)	2.81	2.59	4.8	5.44
t' 90 (min)	7.5	7.63	13.09	12.63
t' 95 (min)	9.16	9.48	15.94	14.9

**TABLE 4.**

<b>CODE 00CW...</b>	<b>221</b>	<b>222</b>	<b>223</b>
3-amino-1-propanol (phr.)	1.4	2.8	5.4
<b>STRESS STRAIN (Die C DUMBELLS, t90+5 @ 170°C., tested @ 23°C.)</b>			
Hard. Shore A2 Inst. (pts.)	60	58	79
Ultimate Tensile (MPa)	18.1	18.0	10.0
Ultimate Elongation (%)	402	319	202
Stress @ 50 (MPa)	1.37	1.24	2.42
Stress @ 100 (MPa)	2.3	2.49	4.31
Stress @ 200 (MPa)	6.2	8.14	9.83
Stress @ 300 (MPa)	12.61	16.5	
300M / 100M	5.5	6.6	
<b>DIE C TEAR (cured tc90+5 @ 170°C., tested @ R.T.)</b>			
Tear Strength (kN/m)	32.6	25.6	30.2
200M / 50M	4.5	6.6	4.1
<b>DIN ABRASION (cure tc90+10 @ 170°C.,)</b>			
Abrasion Volume Loss (mm <sup>3</sup> )	135	109	298
<b>RSA II, TEMPERATURE SWEEP (2°C/min, 60sec soak, 70rad/s, cured tc90+5 @ 170°C)</b>			
Tan delta@ 0°C.	0.591	0.644	0.407
Tan delta@ +60°C.	0.106	0.108	0.080
Loss modulus@ +60°C.	1.176	0.888	1.303
<b>MDR CURE CHARACTERISTICS (1.7 Hz., 3°arc, 60' @ 170°C.).</b>			
MH (dN.m)	41.0	45.6	61.5
ML (dN.m)	10.1	13.3	26.2
ts 1 (min)	0.72	0.48	0.42
ts 2 (min)	0.84	0.6	0.48
t' 10 (min)	1.01	0.69	0.58
t' 50 (min)	4.12	2.4	1.8
t' 90 (min)	11.4	6.66	5.44
t' 95 (min)	13.91	8.28	6.7

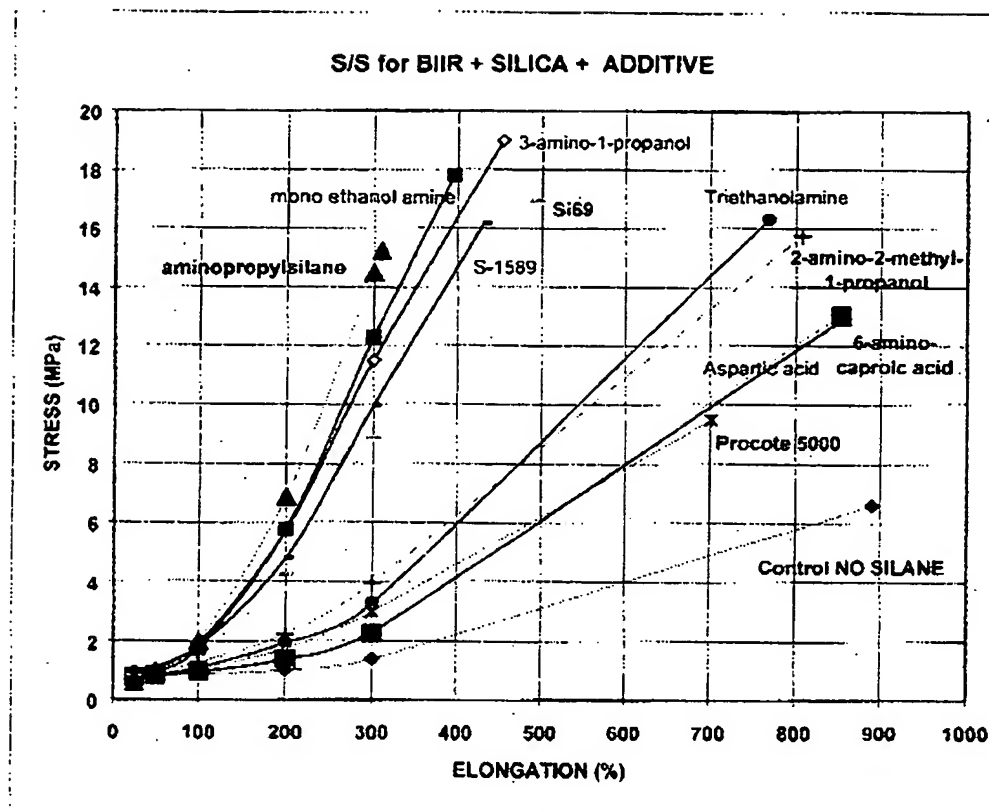
TABLE 5.

CODE 00CW...	218	222	224
Additive	(vii)	(vi)	5-amino-1-pentanol
Additive amount (phr.)	2.2	2.8	3.8
<b>STRESS STRAIN</b> (Die C DUMBELLS, t90+5 @ 170°C., tested @ 23°C.)			
Hard. Shore A2 Inst. (pts.)	58	58	75
Ultimate Tensile (MPa)	18.5	18.0	14.6
Ultimate Elongation (%)	329	319	227
Stress @ 50 (MPa)	1.3	1.24	2.03
Stress @ 100 (MPa)	2.69	2.49	4.16
Stress @ 200 (MPa)	8.5	8.14	12.05
Stress @ 300 (MPa)	16.81	16.5	
300M / 100M	6.2	6.6	
200M / 50M	6.5	6.6	5.9
<b>DIE C TEAR</b> (cured tc90+5 @ 170°C., tested @ R.T.)			
Tear Strength (kN/m)	27.8	25.6	24.9
<b>DIN ABRASION</b> (cure tc90+10 @ 170°C.)			
Abrasion Volume Loss (mm <sup>3</sup> )	90	109	173
<b>RSA II, TEMPERATURE SWEEP</b> (2°C/min, 60sec soak, 70rad/s, cured tc90+5 @ 170°C)			
Tan delta@ 0°C.	0.64	0.64	0.49
Tan delta@ +60°C.	0.10	0.11	0.09
Loss modulus@ +60°C.	1.04	0.89	0.99
<b>MDR CURE CHARACTERISTICS</b> (1.7 Hz., 3°arc, 60' @ 170°C.).			
MH (dN.m)	45.3	45.6	56.7
ML (dN.m)	12.3	13.3	21.4
ts 1 (min)	0.48	0.48	0.42
ts 2 (min)	0.54	0.6	0.54
t' 10 (min)	0.65	0.69	0.59
t' 50 (min)	2.59	2.4	1.78
t' 90 (min)	7.63	6.66	5.72
t' 95 (min)	9.48	8.28	7.42

**CLAIMS:**

1. A process for preparing a filled halobutyl elastomer which comprises admixing a halobutyl elastomer, particles of filler and an additive which has at least one hydroxyl group and one basic nitrogen-containing group.
2. A process according to claim 1, wherein the basic nitrogen-containing group is an amino group.
3. A process according to claim 2 wherein the amino group is a primary amino group.
4. A process according to claim 1, wherein the additive has at least one basic nitrogen containing group and at least one carboxylic acid group.
5. A process according to claim 4, wherein the additive is an amino acid.
6. A process according to claim 1, wherein the additive is an aminoalcohol.
7. A process according to claim 6, wherein the aminoalcohol is a compound of formula  $\text{HO-A-NH}_2$ ; wherein A is a C1 to C20 alkylene group, which may be linear or branched.
8. A process according to claim 7, wherein A is a C1 to C4 alkylene group.
9. A process according to claim 8 wherein the additive is selected from the group consisting of ethanolamine and 3-amino-1-propanol.
10. A process according to claim 1, wherein the amount of additive used results in a nitrogen level in the elastomer of from about 0.1 to about 5 parts per hundred parts of elastomer.
11. A process according to claim 10, wherein the amount of additive used results in a nitrogen level in the elastomer of from about 0.125 to about 1 parts per hundred parts of elastomer.
12. A process according to claim 11, wherein the amount of additive used results in a nitrogen level in the elastomer of from about 0.3 to about 0.7 parts per hundred parts of elastomer.
13. A process according to claim 1, wherein the filler is silica.
14. A process according to claim 1, wherein the filler is carbon black.
15. A process according to claim 1 wherein the resulting filled halobutyl elastomer is cured.
16. A process according to claim 15 wherein the filled halobutyl elastomer is admixed with another elastomer or elastomeric compound before it is subjected to curing.
17. A process according to claim 15, wherein the filled halobutyl elastomer is cured with 0.3 to 2.0 parts by weight of sulfur.

18. A composition comprising a halobutyl elastomer, particles of filler and an additive which has at least one hydroxyl group and one basic nitrogen-containing group.
19. A composition according to claim 18 wherein the amino group is a primary amino group.
- 5 20. A composition according to claim 18, wherein the additive has at least one amine group and at least one carboxylic acid group.
21. A composition according to claim 18, wherein the additive is an aminoalcohol.
22. A composition according to claim 21, wherein the aminoalcohol is a compound of formula  $\text{HO-A-NH}_2$ ; wherein A is a C1 to C20 alkylene group, which may be linear or
- 10 branched.
23. A composition according to claim 22 wherein the additive is selected from the group consisting of ethanolamine and 3-amino-1-propanol.
24. A composition according to claim 18, wherein the amount of additive used results in a nitrogen level in the elastomer of from about 0.1 to about 5 parts per hundred parts
- 15 of elastomer
25. A composition according to claim 18, wherein the filler is silica.
26. A composition according to claim 18, wherein the filler is carbon black.
27. A filled, cured halobutyl elastomer composition prepared by a process according to claim 1.
- 20 28. A filled, cured elastomer composition according to claim 27 in the form of a tread for a vehicle tire.
29. A filled, cured elastomer composition according to claim 27 in the form of an innerliner for a vehicle tire.

**FIGURE 1.**

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**S/S for BIIR + SILICA + ADDITIVE**

